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The solution of the inverse problem in polarization CARS-spectroscopy

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Abstract—An analysis of the solution of the ill-posed inverse problem in polarization CARS is carried out on the basis of mathematical experiments. Smoothing, determination of the number of components and the determination of parameters describing each component are considered. The use of all available experimental and theoretical information is shown to be necessary for correct solution of the problem. The efficiency of the proposed algorithm in the analysis of the complex inhomogeneously broadened lines of chlorocyclohexane is demonstrated.

INTRODUCTION

IN recent years great success has been achieved in the field of non-linear light scattering spectroscopy. Because of the optical non-linearities of a medium one can pass from conventional studies of scattering by molecules excited by thermal oscillations to investigations of scattering by molecules with oscillations phased by coherent laser beams, thus significantly changing the whole picture of scattering.

Non-linear polarization, being a coherent optical response of the medium analyzed, can be described by a non-linear 3rd order susceptibility $\chi^{(3)}_{ijkl}$ [1–6]. In the adiabatic (Born–Oppenheimer) approximation this susceptibility consists of two components, the first related to a resonance coherent response of an oscillatory subsystem of the molecule ($\chi^{(3)R}_{ijkl}$), the second caused by a non-resonance coherent response of the electron subsystem ($\chi^{(3)NR}_{ijkl}$).

In Raman spectroscopy only imaginary components of the corresponding spectral components of the response functions are considered, i.e. of cubic resonance susceptibilities $\chi^{(3)R}_{ijkl}$. In CARS spectroscopy the spectral functions associated with the intensity of the coherently scattered signal contain information on the dispersion of both imaginary and real components $\chi^{(3)}_{ijkl}$ as well as their relative signs [7]. Complete information can be obtained from a set of experimentally measured dispersion curves $I(\Delta w)$ by means of varying the interference conditions between the resonant and non-resonant contributions to the recorded signal, thus changing the polarization of the interacting light waves and also the polarization conditions of the coherent spectra recorded.

In polarization CARS (PCARS) spectroscopy [5, 7] the dispersion of the signal passed through a polarization analyzer is recorded. The intensity is expressed as follows:

$$I(w) \propto |\lambda(w)|^2 = S(w), \tag{1}$$

where $w = w_1 - w_2$, w_1 and w_2 are frequencies of the exciting waves, the frequency w_2 changing smoothly in the scanning mode, passing through the resonance frequency. $\lambda(w)$, a coefficient for m close resonances of the Lorenz type, has the following form:

$$\lambda(w) = \lambda_{NR} + \sum_{k=1}^{m} \frac{\lambda_{Rk}\Gamma_k}{-i\Gamma_k - (w - \Omega_k)}, \tag{2}$$

where λ_{Rk} and λ_{NR} are coefficients depending on the angle ε between the normal to the polarization vector of the non-resonant source and the transmission plane of the

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